

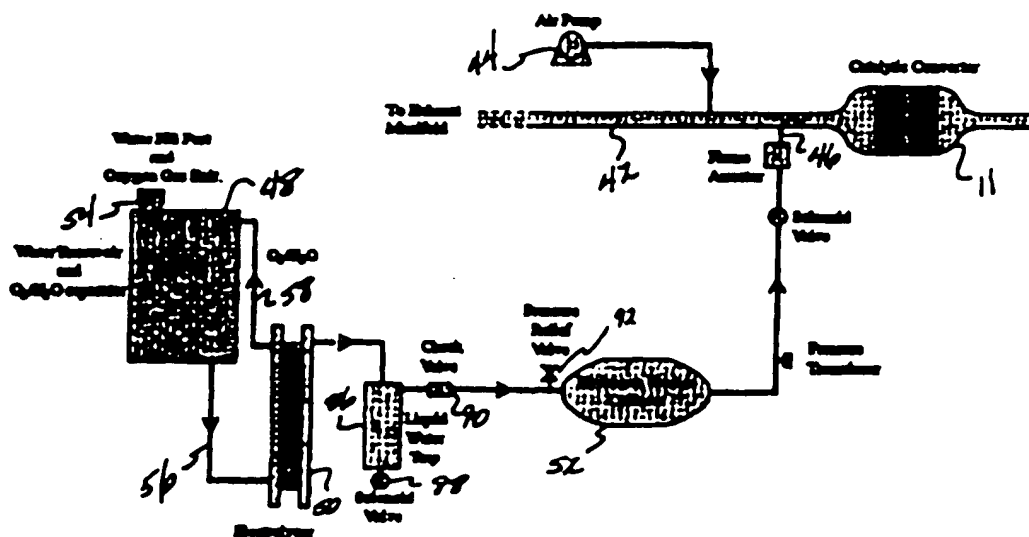
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: F01N 3/20, F02M 25/12		A1	(11) International Publication Number: WO 96/11330
			(43) International Publication Date: 18 April 1996 (18.04.96)
(21) International Application Number: PCT/US95/12912		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GR, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).	
(22) International Filing Date: 6 October 1995 (06.10.95)			
(30) Priority Data: 08/320,171 7 October 1994 (07.10.94) US			
(60) Parent Application or Grant (63) Related by Continuation US 08/320,171 (CON) Filed on 7 October 1994 (07.10.94)		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(71) Applicant (for all designated States except US): TEXAS A & M UNIVERSITY SYSTEM [US/US]; Technology Licensing Office, 310 Wisenbaker, College Station, TX 77843-3369 (US).		5,813,222	
(72) Inventor; and (75) Inventor/Applicant (for US only): APPLEBY, Anthony, John [US/US]; 2810 Briar Creek Court, Bryan, TX 77802 (US).			
(74) Agent: STREETS, Jeffrey, L.; Owen & Associates, P.C., Suite 2900, Five Greenway Plaza, Houston, TX 77046 (US).			

(54) Title: METHOD AND APPARATUS FOR HEATING A CATALYTIC CONVERTER TO REDUCE EMISSIONS



(57) Abstract

A mixture of hydrogen and air is introduced onto the face of the catalytic monolith of a catalytic converter (11) in the exhaust line (42) of a cold internal combustion engine. The hydrogen spontaneously combusts, thereby pre-heating the catalytic converter (11). Pre-heating the catalytic converter (11) significantly improves the effectiveness of the catalytic converter (11) in eliminating undesirable emission of the internal combustion engine. The hydrogen is preferably produced on-board the vehicle using the system. The hydrogen source (52) may also be coupled to the internal combustion engine to be burned by the engine during startup in the absence of gasoline to minimize the production of unacceptable emission while the catalyst is brought up to light-off temperature.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Martinique
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BT	Bhutan	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SI	Slovenia
CH	Switzerland	KZ	Kazakhstan	SK	Slovakia
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	TD	Chad
CN	China	LU	Luxembourg	TC	Togo
CR	Costa Rica	LV	Latvia	TJ	Tajikistan
CZ	Czech Republic	MC	Monaco	TT	Trinidad and Tobago
DE	Germany	MD	Republic of Moldova	UA	Ukraine
DK	Denmark	MG	Madagascar	US	United States of America
EE	Estonia	ML	Mali	UZ	Uzbekistan
FI	Finland	MN	Mongolia	VN	Viet Nam
FR	France				
GA	Gabon				

METHOD AND APPARATUS FOR HEATING A CATALYTIC CONVERTER TO REDUCE EMISSIONS

5

10

15

20

25

30

35

The present invention relates generally to the field of catalysis for the reduction of emissions from internal combustion engines. More particularly, the present invention relates to a method and apparatus for heating a catalyst by spontaneous combustion of hydrogen introduced into the catalyst. Further, the present invention relates to a method of heating a catalyst from a cold condition to light-off comprising the steps of introducing gaseous conditioning agent and a source of oxygen to the catalyst to induce spontaneous exothermic combustion of the conditioning agent by the catalyst. More particularly still, the present invention relates to the conditioning through preheating of a standard three-way or two-way catalytic monolith in a vehicle powered by an internal combustion engine, such as an automobile.

40

45

The control and suppression of unwanted emissions created by the operation of an internal combustion engine is a primary consideration for engine designers and vehicle manufacturers because of nearly world-wide governmental requirements regarding acceptable emission levels. Over eighty percent (80%) of the unacceptable emissions or pollutants created by internal combustion engines equipped with catalytic converters occur during cold start operations. These pollutants are emitted for a period of one to three minutes after cold engine starting, in large part because that is the time period required for the catalyst to reach an efficient operating temperature. Therefore, even though the engine exhaust is flowing through the catalytic converter, until the exhaust heats the catalytic converter to its operating range from engine start up, the exhaust flow is only slightly catalyzed during that time period.

In order to meet governmental emission standards for internal combustion engine exhaust, a catalytic converter is located in the exhaust stream of the engine. The converter typically includes a canister holding a suitable catalyst, such as a three-way catalytic converter (TWC) catalyst monolith, that will oxygenate unburned, unacceptable components in the exhaust stream including hydrocarbons ("HC"), their partially oxidized derivatives such as aldehydes and carbon monoxide ("CO"), and at the same time reducing nitrogen oxides ("NO_x"), after almost stoichiometric fuel burn with oxygen in the cylinders of the engine. The exhaust gas is passed through the catalyst monolith, thereby completing the oxygenation of unburned HC and CO, and the reduction of NO_x in the exhaust to convert these unacceptable emissions into acceptable emissions. Certain unacceptable emissions in the exhaust stream, including unburned hydrocarbons and carbon monoxide, require an oxidation reaction to destroy them so that they end up as the corresponding oxides, e.g. water and carbon dioxide. On the other hand, NO_x requires a reduction reaction to develop N₂ and O₂. In fact, the O₂ product of this reduction contributes to the oxidation of the HC and CO in the exhaust.

TWC catalysts are currently formulated and designed to be effective over a specific operating range of both lean and rich fuel/air conditions and a specific operating temperature range. These particulate catalyst compositions enable optimization of the conversion of HC, CO, and NO_x. This purification of the exhaust stream by the catalytic converter is dependent on the temperature of the exhaust gas and the catalytic converter works optimally at an elevated temperature, generally at or above 300°C. The time span between when the exhaust emissions begin (i.e., "cold start"), until the time when the substrate heats up sufficiently for the catalyst to work efficiently, is generally referred to as the light-off time. Light-off temperature is generally defined as the temperature at which fifty percent (50%) of the emissions from the engine are being converted as they pass through the catalyst.

The conventional method of heating the catalytic converter is to heat the catalyst by contact with high temperature exhaust gases from the engine. This heating, in conjunction with the exothermic nature of the oxidation reaction occurring at the catalyst, will bring the catalyst to light-off temperature. However, until the light-off temperature is reached, the exhaust gas passes through the catalyst relatively unchanged. In addition, the composition of the engine exhaust changes as the engine heats from the cold start temperature, and the catalyst is designed to work best with the composition of the exhaust stream present at the normal elevated engine operating temperature.

There have been several attempts to shorten or avoid the time between cold start and light-off of the catalytic converter. Current techniques employ one or more of the following methods: electrical heating of the exhaust gases and/or of the catalytic converter itself; thermal insulation; multi-chambered configurations of the catalytic converter; and/or placing the catalytic converter adjacent to the engine for heating. All of these methods have drawbacks and limitations.

Placing the catalytic converter almost immediately adjacent to the engine is not feasible because of the tendency to overheat the catalyst with resulting accelerated degradation of the catalyst due to excessive heat. Thermal insulation is also not an acceptable option because of the same problems, especially during operation under maximum operating temperature ranges.

Electrical heating of catalytic converters ("EHC") has been a popular proposed method of attempting to preheat the catalyst monoliths. Limitations on the equipment and process, however, affect the utility of this method. The primary limitation on electrical preheating is the electrical energy required by the heater. The typical car battery is not a practical power source to supply the electrical power because the electrical load on the vehicle battery during the period required may exceed the rated battery output. In any event, the load placed on a typical 12 volt vehicle battery will shorten the lifetime of the battery. Also, there is a measurable delay between the time the operator of the vehicle places the ignition switch in the "on" position and the time the heater brings the catalyst to light-off temperature.

Typically, in the interval between start up and light-off, the exhaust stream is oxygen deficient. Because the catalyst requires oxygen to complete the catalytic reaction, supplemental air must be blown over the catalyst. Even when using a secondary air flow to overcome oxygen deficiency, the secondary air flow must be closely controlled to avoid an excess of oxygen, in which case the catalytic converter is less effective in reducing NO_x . However, it should be noted that NO_x contributes a very small portion of unacceptable emissions when an engine is cold; most of the emissions that must be dealt with comprise HC and CO and the like.

An alternative to battery powered electrical heating has been to decrease the strain on the power supply by supplying the power directly from an alternator rather than directly from the vehicle battery. An alternator powered, electrically heated catalyst ("APEHC") still requires a 5 to 10% increase in battery capacity to cope with the EHC start-up scenario. Even with the APEHC system, there still is a concern with respect to battery capacity because electric heating is needed for an extended period of time, i.e., more than 25-30 seconds. In addition, the maximum alternator power output required in the APEHC system requires a complicated switching

mechanism and an altered alternator speed between 3,000 and 4,500 rpm during the heat up time period, and the alternator must be oversized.

5 The multi-chamber configurations of catalytic converters generally conform to one of two theories. In one multi-chamber configuration, a small portion of catalyst known as a "starter catalyst" is positioned upstream from the primary catalyst. This "starter catalyst" is generally closer to the exhaust manifold. This location, in conjunction with a smaller thermal mass associated with its smaller size, causes the catalyst to heat much more quickly than a single catalyst. This configuration, however, is generally unacceptable because the starter catalyst in the exhaust stream
10 creates a higher back pressure which reduces the overall engine efficiency and robs the engine of power output.

Another method of providing multiple chambers in the exhaust flow includes a first catalyst having low temperature characteristics used only during cold start conditions, and, after the catalyst temperature ranges rise to a selected elevated level,
15 the exhaust gas flow is switched to pass through the conventional catalytic converter configuration. A variation of this approach is to run all cold start emissions through a separate absorber (such as zeolite or a metal sieve-type substance) wherein unacceptable emissions are captured and later released back into the exhaust stream. This method, however, is impractical because of the complicated switching
20 mechanism used to divert flow to the absorber, the size and space requirements of the absorber, and the impracticality of releasing the unacceptable emissions from the absorber back into the exhaust stream.

Finally, one method runs the engine excessively rich in the cold start condition and ignites the resulting super-rich mixture to directly heat the catalyst.
25 This approach has proved wholly unreliable and has other serious drawbacks, including reduced engine and catalyst life.

To date, there has not been a catalytic converter heating system which gives almost instantaneous heating of the catalytic converter without the inherent drawbacks stated above.

30 Thus, there remains a need for an improved catalytic converter system that reduces ineffective catalytic action immediately after cold start-up of an engine. Such a system must be simple and must not reduce the rated lifetime of the engine, the catalytic converter, or the battery components of the vehicle.

35 SUMMARY OF THE INVENTION

Accordingly, the present invention provides a method and apparatus for reducing undesirable emissions from an internal combustion engine by using a gas

that spontaneously combusts in the presence of a catalyst to heat the catalyst into its operating range in a minimal amount of time. In a preferred embodiment, the catalyst is heated by providing a controlled flow of hydrogen and a source of oxygen, such as air, into the exhaust stream, preferably at a point between the engine manifold and the catalytic converter. The hydrogen combusts with the oxygen in the presence of the catalyst to produce water. This exothermic combustion provides localized heat at the catalyst which raises the temperature of the catalyst material.

The hydrogen is preferably supplied from an electrolyzer on board the vehicle which is supplied with DC power from the vehicle's alternator via an AC/DC converter. Such an electrolyzer produces hydrogen and oxygen from water. The oxygen so produced is vented while the hydrogen is accumulated during non-cold engine operations for release during engine start up and cold operating conditions. Sufficient hydrogen may be stored in a hydride such as LaNi_5 or FeTi or may be accumulated in a pressure tank or other container such that there is hydrogen for several starts. The source of water may be distilled water; however, windshield washer fluid may also be used to eliminate the need for another storage facility for water.

It is well recognized by those of skill in the art of catalytic converter design that some monolith compositions more quickly and easily reach light-off temperatures than others. Consequently, the present invention is especially advantageous when applied to catalysts that are difficult to bring to light-off temperature by applying a small layer or film of a material that is more reactive to hydrogen and is thus more rapidly heated by spontaneous combustion of hydrogen. Such a layer or film could be applied to a face of the slow-heating monolith or could be distributed throughout the converter, as design requirements dictate. Rapid exothermic heating of the applied catalyst quickly brings the entire structure to a temperature at which normal, efficient catalytic action occurs.

In another preferred embodiment of the invention, a small amount of stored hydrogen may be supplied to the fuel injection system of the vehicle to assist in cold starts. This allows instant firing of the engine, even with fuels with low vapor pressure, such as methanol, ethanol, or low Reid vapor pressure gasoline.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features and advantages of the invention will become apparent from the following description when read in conjunction with the accompanying drawings, wherein:

Figure 1 is a schematic diagram of the apparatus of the present invention for heating a catalytic converter;

Figure 2 is an exploded view of a preferred electrolyzer that may be employed in the present invention;

5 Figure 3 is a schematic of a hydrogen capturing and handling detail of the system of the present invention;

Figure 4 is a schematic of a test setup to assist in the determination of the ideal parameters of a system functioning in accordance with the teachings of the present invention;

10 Figure 5 is a sectional view of a simplified representation of a catalytic converter monolith showing air and hydrogen flow in the axial direction;

Figures 5A, 5B, 5C, and 5D are temperature plots of the variation of temperature with time along the axial length of a catalytic converter monolith for different hydrogen concentrations in a flowing gas stream;

15 Figure 6 is a sectional view of a simplified representation of a catalytic converter monolith for temperature measurements along the major radial direction in the monolith;

Figures 6A, 6B, 6C, and 6D are temperature plots of the variation of temperature with time along the major radial direction of a catalytic converter monolith for different hydrogen concentrations in a flowing gas stream; and

20 Figure 7 is a schematic diagram of the apparatus of the present invention depicting a system for the combustion of hydrogen for cold startup assist for an internal combustion engine.

25 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides a method and apparatus for thermally conditioning a catalyst in order to enhance the conversion of unacceptable emissions emanating from an internal combustion engine into water and other acceptable emissions.

30 Referring first to Figure 4, the schematic depicts the general configuration of a conditioning system 10 for catalytically enhancing emission reactions. The system 10 includes a catalytic converter 11, a metered hydrogen supply 13, and a metered air supply 14. Additionally, one or more thermocouples 11a are implanted at various positions along the radial and axial directions of the catalytic converter. The
35 thermocouples are connected to a data logger 12, capable of recording the temperature of the catalyst as a function of time. The system 10 of Figure 4 is particularly useful in demonstrating the efficacy of the present invention and for

determining the optimum flow rates of hydrogen and air and other system parameters.

The flows of hydrogen and air from supplies 13 and 14 are controlled by valves or regulators 15 and 16, respectively. The regulator 16, which controls the air supply, is preferably coupled to a rotameter 17, which measures the air flow rate. The metered air then flows to a mixing chamber 20. The flow of hydrogen, which is controlled through a valve or regulator 15 and regulated by an electronically controlled mass flow controller 18 in conjunction with the controller 19, is also delivered to the mixing chamber 20.

In the mixing chamber 20, the hydrogen and air are thoroughly mixed before passing through a three way valve 21. The three way valve 21 operates to provide a bypass of the hydrogen and air mixture directly to the surrounding environment via an outlet 23 or to a conduit 22, through which the hydrogen and air mixture are introduced into the catalytic converter 11. This configuration allows for a widely varying flow of hydrogen and air to a catalytic converter to determine the proper hydrogen/air ratios for practicing the present invention.

Figure 5 depicts a catalytic converter monolith 30 in the catalytic converter 11 that may be conditioned with the present invention. Arrows 40 represent the stream of air and hydrogen passing through conduit 22 and into contact with the monolith 30 along a central axis 37. Points 31a, 31b, 31c, 31d, and 31e represent the location of thermocouple probes, as generally represented by 11a in Figure 4, for the measurement of temperatures along the axial or flow direction into the catalytic converter.

Figure 6 depicts the radial distribution of a plurality of probes 33a, 33b, and 33c within the monolith 30. Below are listed some results for variously changing parameters as determined by the distribution of the thermocouple probes 31a-31e and 33a-33c.

Figures 5A-D, inclusive, depict test results of the distribution of temperatures detected by the thermocouples distributed as shown in Figure 5 for varying concentrations of hydrogen. Similarly, Figures 6A-D, inclusive, depict test results of the distribution of temperatures detected by the thermocouples distributed as shown in Figure 6 for the same concentrations of hydrogen. These plots clearly show the effectiveness of the heating on the face of the catalytic converter monolith and will assist those of skill in the art in selecting optimum fluid flow rates in a particular application.

Figure 1 shows an overall system of the present invention. In this system, the catalytic converter 11 is located in an exhaust line 42 from a vehicle's exhaust

manifold, as shown. The exhaust line 42 is provided with air from an air pump 44 and hydrogen from a hydrogen inlet line 46. The air pump could be any suitable air source, such as a receiver, for injecting air into the exhaust line at suitable pressure and volumetric flow rate to achieve the ideal air/hydrogen ratio mixture.

5 The hydrogen source portion of the system of Figure 1 provides another feature of the present invention. The major components of the system include a reservoir 48, an electrolyzer 50, and a hydrogen storage cylinder 52. As shown in Figure 1, the electrolyzer 50 may preferably comprise a plurality of stacked identical cells 51. The reservoir 48 serves both as a water reservoir and as a separator for
10 oxygen and water. In a preferred embodiment, the reservoir 48 may be a vehicle's windshield washer fluid storage container. A port 54 permits the introduction of water into the reservoir and also serves as a vent to atmosphere for oxygen. Water flows by gravity drain or is pumped from the reservoir 48 to the electrolyzer 50 via a drain line 56. As the electrolyzer develops hydrogen and oxygen, the oxygen and
15 entrained water flows naturally back to the reservoir 48 via a return line 58.

 The next major component of the hydrogen source is the electrolyzer 50, shown in greater detail in Figure 2. In the following description of the electrolyzer 50, the materials of construction referred to as "preferred" are the materials actually
20 used in a test device to prove that the invention would work for its intended purpose. In commercial production models of the present invention, where possible, less expensive materials will be used throughout, such as carbon steel for titanium where possible, and plastic such as polypropylene where heat and stress will permit the use of such material.

 The electrolyzer 50 may be referred to herein as a proton exchange membrane (PEM) electrolyzer 50. The proton exchange membrane itself may prove corrosive in
25 this environment in contact with certain substances, thus requiring the careful selection of the materials of construction of the electrolyzer. For example, the PEM should only contact carbon or graphite. However, those of skill in the art will readily recognize where less exotic materials than those listed in the following discussion
30 that are located away from the PEM material itself and the oxygen electrode catalyst can be readily employed without penalty. For example, graphite will be the material of choice in certain structural elements, and not some obvious candidates such as copper, aluminum, or iron, which can corrode thus forming ions that can poison the oxygen and/or hydrogen electrode catalysts.

35 The PEM electrolyzer 50, formed as a stack as shown in Figure 2, includes a pair of endplates 60 and 62. The endplates 60 and 62 are preferably comprised of titanium. Adjacent the top endplate 60 is an anodic cell frame 64. The cell frame 64

is preferably a carbon fiber-filled Teflon sheet, sold under the trademark Zymaxx by Du Pont. The cell frame 64 retains a 1:1 molar ratio of iridium and ruthenium dioxides ($\text{IrO}_2/\text{RuO}_2$) as the anodic electrocatalyst. The cell frame 64 also includes a plurality of flow ports 66 to permit the supply of reactant (water) and/or removal of electrolysis products (hydrogen or oxygen gases). Below the cell frame 64 is an expanded titanium metal current collector (flow field) 68 of the type available from Exmet Corp. An anode substrate 70 is preferably a porous titanium plate measuring 2.49" x 2.49" x 0.05". Below the anode substrate 70 is a proton exchange membrane 72, cut from a sheet of Nafion 117 from Du Pont which serves as a solid electrolyte material and which is about 175 μm thick.

Figure 2 depicts a gasket 74, one of perhaps several installed where required. Gaskets 74 are stamped from 0.033" thick fluorosilicone sheet (Viton) and from 0.005" thick unsintered PTFE sheet. The electrolyzer 50 further includes a cathode substrate 76 like the anode substrate 70 and an expanded titanium flow field 78 like the titanium flow field 68.

Finally, the PEM electrolyzer 50 includes a cathodic cell frame 80 formed of polychlorotrifluoroethylene (PCTFE) sheet, sold under the trademark KEL-F by Afton Plastics. The cathodic cell frame 80 retains a fuel cell gas diffusion electrode containing high surface area colloidal platinum, supported on platinum black, having a platinum loading of 4.0 mg/cm^2 as the cathodic electrocatalyst layer.

As shown in Figure 2, the various components of the PEM electrolyzer are stacked together and retained with a plurality of tie rods 82, preferably 16 such tie rods. Stainless steel tubing is then screwed into four threaded ports on one of the titanium endplates. These ports are the water inlet port 56, the oxygen outlet port 58, and a pair of hydrogen outlet ports 84. To minimize electrical contact resistances, the titanium endplates 60 and 62 and the expanded titanium metal current collectors 68 and 78 may be electroplated with a thin film of gold.

The cathode and the anode of the electrolyzer are of special construction. The cathodic electrode structure for hydrogen evolution is fashioned from commercially available fuel cell gas diffusion electrodes from E-TEK of Natick, Mass. This structure comprises a hydrophobic gas diffusion layer on a carbon cloth backing, which acts as a support for the active hydrophilic electrocatalyst layer. This active layer contains high surface area colloidal platinum ($\sim 100\text{m}^2/\text{g}$), supported on carbon black (60 wt % Pt on C), yielding a platinum loading of 4.0 mg/cm^2 . The cathodic electrode structure, having an area of 40 cm^2 , was hot-pressed onto one side of a segment of precleaned Nafion 117 PEM material. Hot-pressing was carried

out between the plates of a hot-press, elevated to 200°C for 60 seconds, and using a force of 15,000 pounds.

For the anodic electrocatalyst layer, a 1:1 molar ratio of iridium and ruthenium chlorides are dissolved in about 8 ml of concentrated HCl and heated to almost dryness. The resulting chlorides are then dissolved in isopropanol to make an ink-like coating. A porous titanium plate, 0.05" thick, of about 50% porosity, made from sintered titanium spheres of about 0.005" in diameter from Astro Met of Cincinnati, Ohio, is etched in 12% HBF₄ for 60 seconds and rinsed with isopropanol. This substrate is then coated with the ink-like mixture and the solvent evaporated under low heat of about 90°C. The coating and drying procedure is repeated several times, then the electrode is heated in a furnace at 400°C for 10 minutes in ambient air. The coating, drying and furnace treatment is repeated twice more, but with a final baking time of two hours instead of 10 minutes.

Returning to Figure 1, in addition to the reservoir 48 and the electrolyzer 50, the system includes a hydrogen storage cylinder and various supporting components. These components include a liquid water trap 86 to eliminate most of the entrained water from the hydrogen from the electrolyzer, a solenoid valve 88 to blow out the trap, a check valve 90, and a pressure relief valve 92 to protect the system against overpressurization. Figure 3 depicts additional details and a preferred arrangement of the hydrogen gas handling and capture system.

As previously described, the electrolyzer 50 includes a proton exchange membrane in its stacked construction so that generated oxygen is vented to the water source reservoir and the hydrogen generated can be accumulated at pressure. Prior to operation, the system of Figure 3 permits purging with an inert gas, such as nitrogen. For safety reasons, all air is first removed from the system by attaching a nitrogen gas feedline at a purge gas inlet 94 downstream of a check valve 90. During the purging operation, the hydrogen storage cylinder or vessel 52, preferably made of a metal hydride, is detached at a quick disconnect 96. This operation effectively seals both the vessel 52 and a gas line 98, to keep the purge gas out of the vessel 52. The remainder of the system is then purged from the purge gas inlet 94 through a back pressure regulator 100.

To charge the system with hydrogen, a needle valve 102 between the storage vessel 52 and the back pressure regulator 100 is shut. Hydrogen gas generated by the electrolyzer is processed through a four-stage process to remove entrained water (liquid or vapor) and any oxygen contaminant from the hydrogen stream before storage. The first step involves removal of a small amount of entrained liquid water coming from the electrolyzer in the hydrogen gas. This entrained liquid water is

removed without a pressure loss by means of the entrained liquid water trap 86. The second step involves cooling the hydrogen gas stream from the electrolyzer temperature to ambient in a condensing coil 104. The electrolyzer is typically at least 20°C above ambient, with the exact temperature depending on electrolyzer operating conditions. This second step condenses a substantial portion of the water vapor in the hydrogen gas stream. This condensed water could absorb a significant amount of alcohol, which may be present during operation using windshield washer fluid as the electrolyzer reactant feed. The condensate is collected in a condensate collector 106 and removed through a drain valve 108.

At this point, the hydrogen gas stream is still saturated with water vapor, but now at a lower temperature. This saturated gas stream is next passed into a zeolite-filled gas drier 110. This drier absorbs water vapor and any alcohol vapor present when using a windshield washer fluid feed. Any oxygen contaminant present in the hydrogen gas stream is then eliminated in a catalytic recombiner or oxygen eliminator 112 to reduce it to water. Final clean-up of the hydrogen gas stream is accomplished in a second zeolite absorber bed in a polishing drier 114. The polishing drier removes traces of water produced by the catalytic recombiner 112.

The hydrogen gas handling system of Figure 3 is designed for relatively short term operation; longer term operations, for example 100,000 miles, would utilize other methods of water removal known in the art. A satisfactory metal hydride hydrogen storage unit is available from Hydrogen Consultants of Littleton, Colorado. Such an available unit can store 30 liters of hydrogen, which can be delivered at 30-45 psig, with recharging using hydrogen gas at 100-200 psig.

As previously described, it has been found that the introduction of a relatively small percentage of hydrogen in the air stream of a typical automobile gas exhaust provides nearly spontaneous heating of a major portion of a face 32 (Figure 5) of the catalyst material almost immediately following ignition in the internal combustion engine providing the exhaust gas. This heating along the face 32 of the converter is fortuitous because it has been found that the most effective site for providing local heating is along and near the upstream face 32 of the catalyst monolith 30. In fact, where the monolith 30 is made of a material that heats slowly when used in association with the present invention, the face 32 may comprise a more reactive catalytic material to bring the entire catalytic converter to light-off more quickly.

In addition, the heat supplied by the spontaneous combustion of the hydrogen in the presence of the catalytic converter 30 produces only a small quantity of water as a product of the reaction, which does not degrade the performance of the catalytic converter.

A system 10 built in accordance with the present invention as depicted in Figures 4, 5, and 6 have provided preferred parameters of air and hydrogen flow. The air flow rate, depending on engine size and tuning parameters, typically falls in the range of 40 to 250 liters per minute (lpm). The ideal range is between 80 and 200 lpm, depending on engine size. Effective concentrations of hydrogen for these flow rates are one to twenty-eight volume percent, with a preferred range of five to eighteen percent. The ideal range of hydrogen concentration, again depending on engine size, has been found to be eight to fifteen percent. For example, at 150 lpm flow rate across the catalytic converter, the ideal range for hydrogen concentration in that flow is 12 to 13 volume percent. Under those conditions, light-off temperature at the face 32 is reached in about one second. At 90 lpm and at 8.5 to 11 volume per cent hydrogen, light-off is achieved in about two seconds.

The power consumption at the catalyst varies depending on the flow rate and the concentration of hydrogen. For example, at a flow rate of thirty to fifty lpm and a concentration of 10-11 $\frac{1}{2}$ volume percent hydrogen, the power required to heat the monolith to light-off is approximately 1.5 watt hours. Similar results in an EHC unit require approximately 10 to 15 watt hours.

The present invention is also suitable for use in low ambient temperature conditions, as low as -7°C or lower. Depending on the active catalyst compositions used, the amount of time required to achieve light-off may double. In those conditions, it may be desirable to add a small electrical heater, which would be much smaller than an EHC heater and require only about 200 watts of power, in order to achieve the results at normal ambient temperatures.

Finally, Figure 7 depicts an on-board hydrogen ignition assist system of the present invention. A source of hydrogen, such as an electrolyzer as before or any suitable means, fills the hydrogen storage cylinder 52. An ignition supply line 120 taps off the hydrogen line to a control valve 122. The control valve 122 controls the supply of hydrogen into an engine ignition 124. The engine ignition 124 includes the fuel, air, and electrical components for an internal combustion engine 126. Thus, the hydrogen can be supplied at any convenient location so that it is injected into the cylinders of the engine 126. For example, hydrogen under pressure can be supplied to the intake manifold where there is already a fuel/air mixture (during the inlet cycle), or the hydrogen can be mixed with air before it goes into the engines fuel injection system, or other means.

The preferred system of Figure 7 turns the internal combustion engine 126 into a hydrogen fuel injected engine for the first few seconds of start-up, before any gasoline is introduced into the engine. This way, the catalytic converter can be

brought to light-off while the engine is producing not undesirable emissions. Then, when gasoline is finally injected into the system, the catalytic converter is heated to efficient operating temperature.

5 Expanded fuel gases are collected in an output manifold 128 and flow into the exhaust line 42. An ignition control 130 provides control signals to the control valve 122 for the introduction of hydrogen and to the engine ignition 124 to coordinate hydrogen introduction during cold start operations. The on-board hydrogen ignition assist system functions with or without the catalyst conditioning system but is preferably included with such a system since they may both use the hydrogen
10 generation and on-board storage.

I Claim:

1. A method of heating a catalyst from a cold condition to light-off comprising the steps of introducing gaseous conditioning agent and a source of oxygen to the catalyst to induce spontaneous exothermic combustion of the conditioning agent by the catalyst.
5
2. The method of claim 1, wherein the conditioning agent is hydrogen and the method comprises the step of storing gaseous hydrogen within a hydrogen storage vessel prior to the step of introducing hydrogen.
3. The method of claim 2 further comprising the step of electrolyzing
10 water to produce hydrogen to be stored.
4. The method of claim 3 further comprising the step of purifying the hydrogen produced in the step of electrolyzing by removing water and other impurities from the hydrogen.
5. The method of any preceding claim, wherein the source of oxygen
15 comprises air.
6. The method of claim 3, wherein the step of electrolyzing is carried out on-board a vehicle driven by an internal combustion engine.
7. The method of claim 6 further comprising the step of providing
20 electrical power for the step of electrolyzing from an AC to DC converter that is powered from an alternator driven by the engine.
8. An apparatus for conditioning a catalyst within a catalytic converter, which apparatus comprises:
 - a. a conditioning agent storage container; and
 - b. a conduit coupling the conditioning agent storage container to the
25 catalytic converter.
9. An apparatus for the reduction of the cold-start emissions from an internal combustion engine with an exhaust line and a catalytic converter in the exhaust line, wherein the conditioning agent storage container comprises a hydrogen
30 storage container and the conduit provides fluid flow path coupling the hydrogen storage container to the exhaust line to direct hydrogen into the catalytic converter.

10. An apparatus according to Claim 8 or 9 further comprising:
- a. a source of water;
 - b. an electrolyzer coupled to the source of water to electrolytically produce hydrogen; and
 - c. a fluid flow path to direct hydrogen produced in the electrolyzer into the conditioning agent storage container.
11. An apparatus according to claim 10, wherein the electrolyzer comprises a plurality of cells.
12. An apparatus according to claim 10 or 11, wherein the source of water comprises a vehicle's windshield-washer fluid reservoir.
13. An apparatus according to any one of Claim 10 to 12 further comprising an alternator driven by an internal combustion engine to develop AC power and an AC/DC converter electrically coupled to the alternator to provide DC power to the electrolyzer.
14. An apparatus according to any one of Claims 8 to 13 further comprising a hydrogen purifier in the fluid flow path.
15. An apparatus according to Claim 14, wherein the hydrogen purifier comprises a water trap to remove water entrained with the hydrogen and an oxygen eliminator to remove oxygen contaminant that may be present with the hydrogen.
16. An apparatus according to any one of Claims 9 to 15 further comprising a source of air connected to the exhaust line.
17. An auxiliary system for an internal combustion engine having a fuel and air intake, combustion cylinders, and an exhaust, the auxiliary system comprising the apparatus of any one of Claims 8 to 16 and further comprising:
- a. a control valve between the conditioning agent storage cylinder and the engine to selectively provide conditioning agent to the engine when the control valve is open; and
 - b. an ignition control coupled to the control valve to open the control valve for a predetermined period of time during the start-up of the engine.

18. The system of Claim 17, wherein the control valve is in fluid communication with the intake of the engine.

19. The system of Claim 17, wherein the control valve is in fluid communication with the cylinders of the engine.

5 20. A system for the reduction of the cold-start emissions from an internal combustion engine with an exhaust line and a catalytic converter in the exhaust line, the engine further having a fuel and air intake and combustion cylinders, the system comprising:

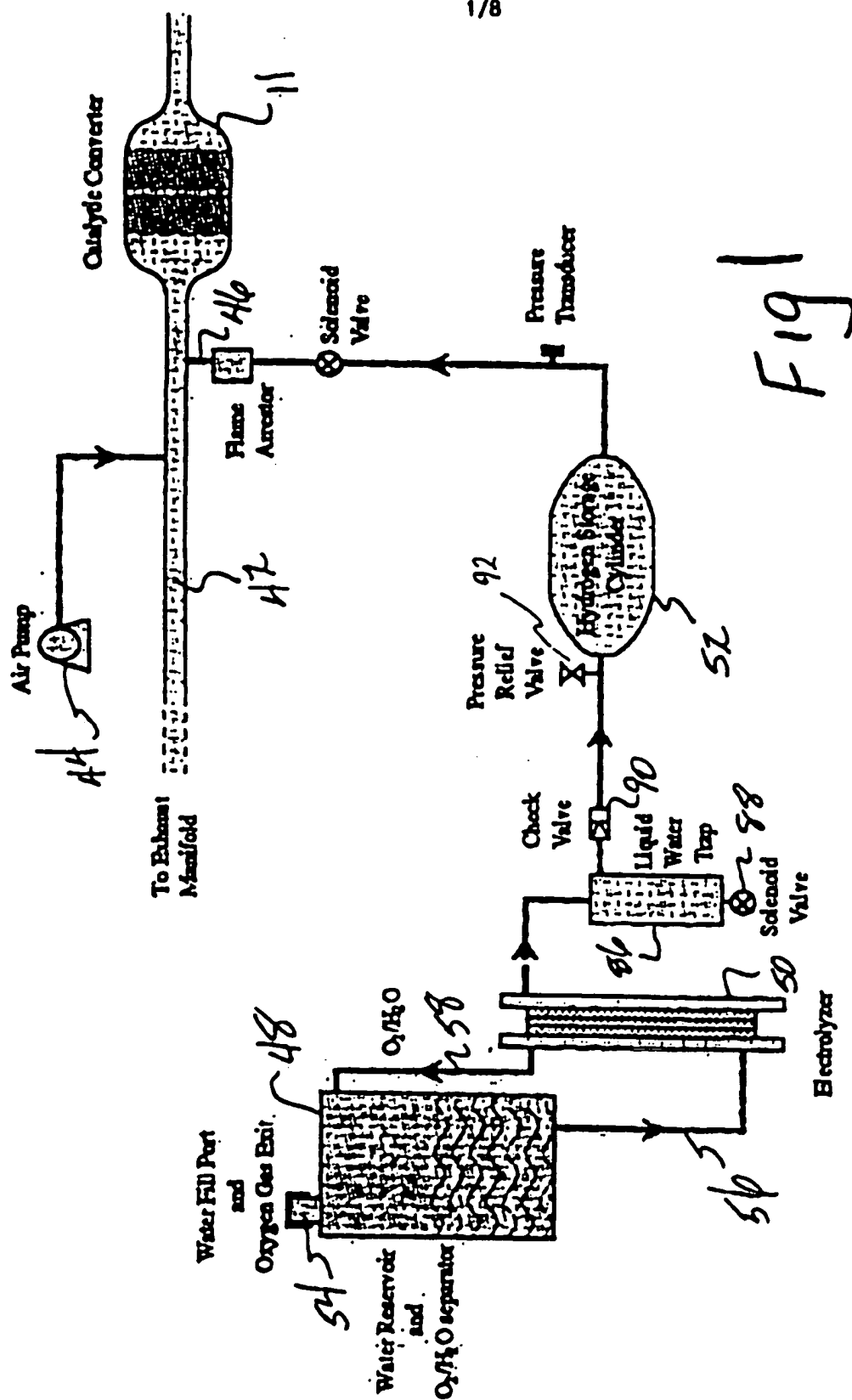
- 10 a. the apparatus of any one of Claims 8 to 16, wherein the fluid flow path couples the conditioning agent storage container to the catalytic converter through the exhaust line to direct conditioning agent into the catalytic converter;
- b. a source of oxygen connected to the exhaust line; and
- 15 c. a controllable port from the conditioning agent storage container to the engine wherein conditioning agent from the storage container is ported to the engine for a controlled period of time during start-up of the engine.

21. An apparatus according to any one of Claims 8 to 16 or a system according to any one of Claims 17 to 20, wherein the catalytic converter comprises:

- 20 a. a monolith of a first catalytic material, the monolith having an inlet face; and
- b. a layer on the inlet face, the layer made of a second catalytic material that heats more rapidly in the presence of hydrogen and oxygen than the first catalytic material.

25 22. An apparatus for thermally conditioning a catalyst within a catalytic converter, which apparatus comprises:

- a. a conditioning agent storage container; and
- b. a conduit coupling the conditioning agent storage container to the catalytic converter.



2/8

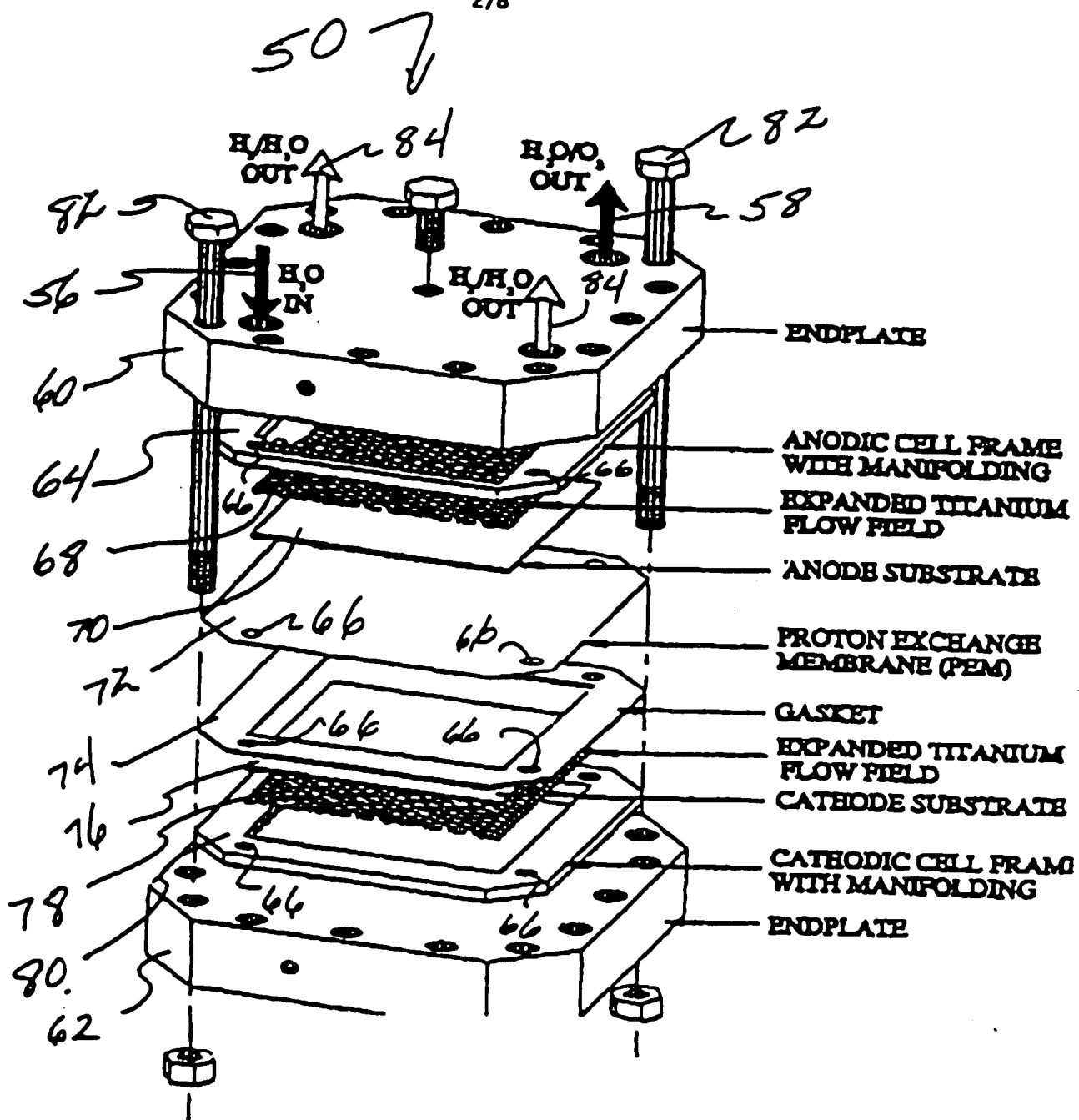


Fig 2

3/8

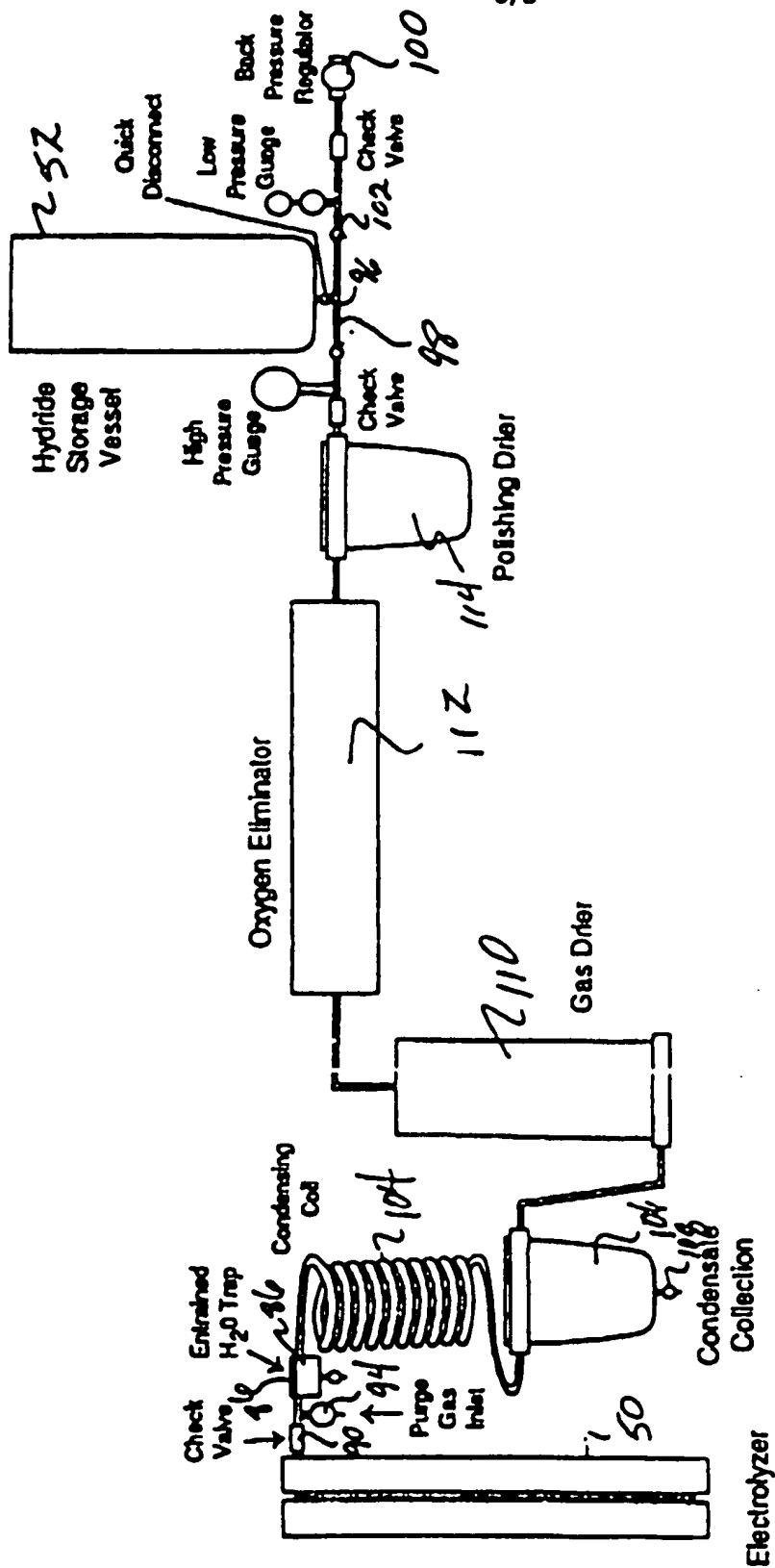
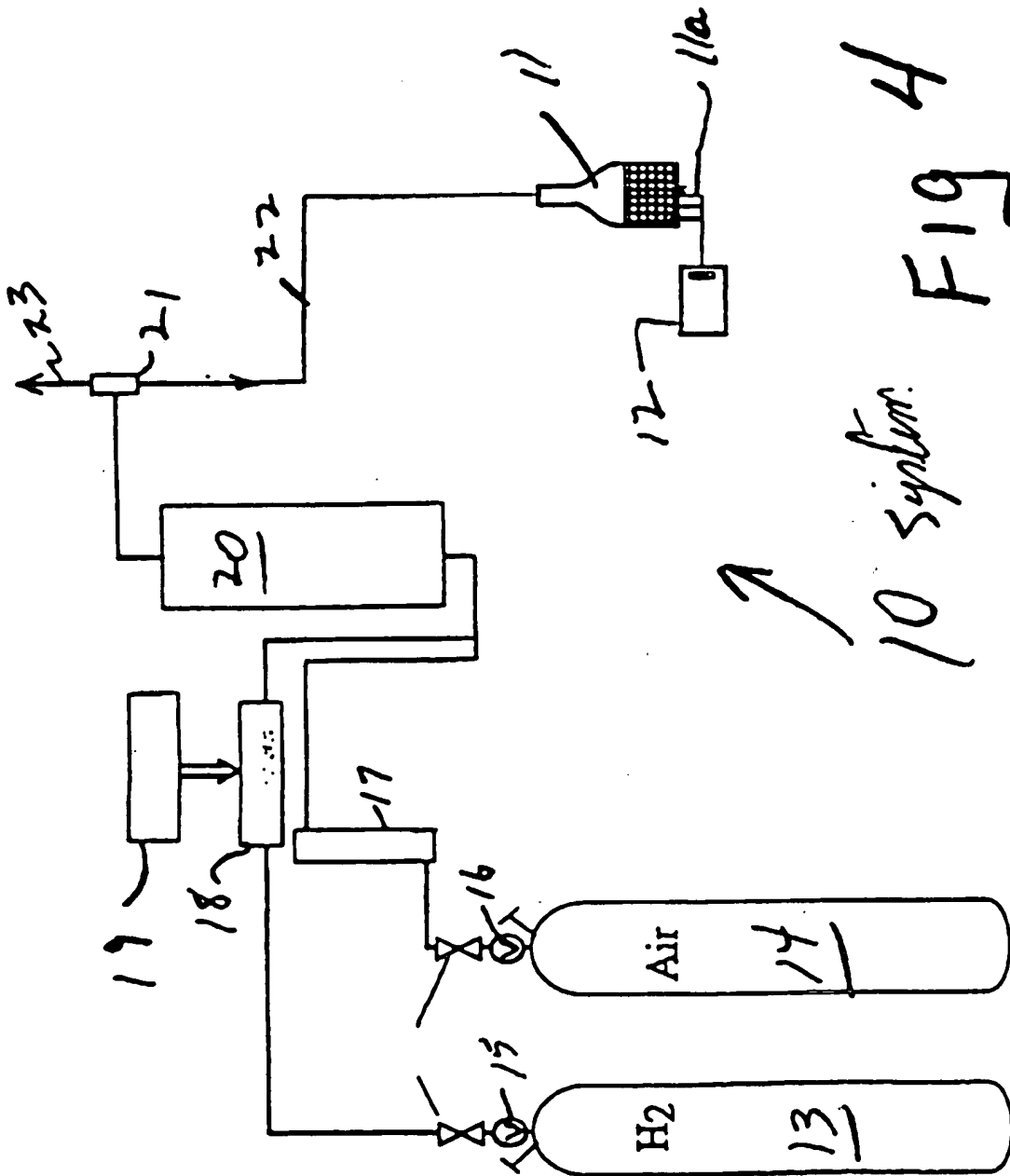


Fig 3



10 system
Fig 4

5/8

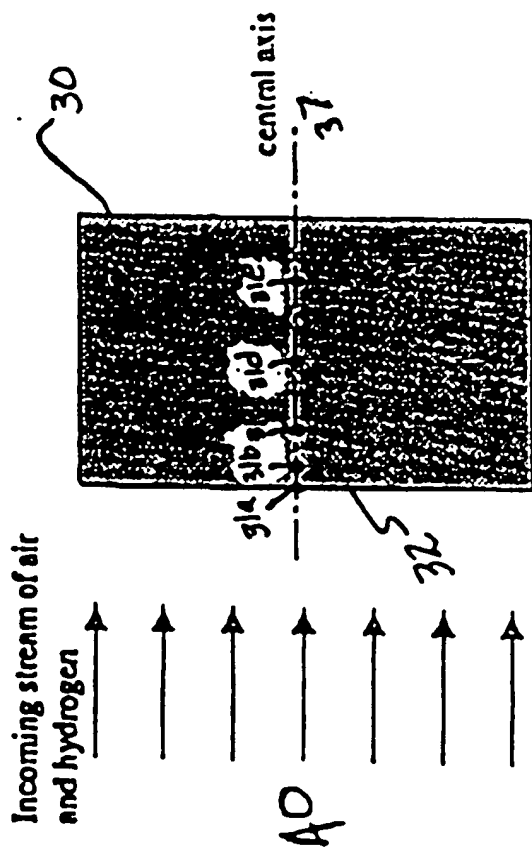


Fig. 5

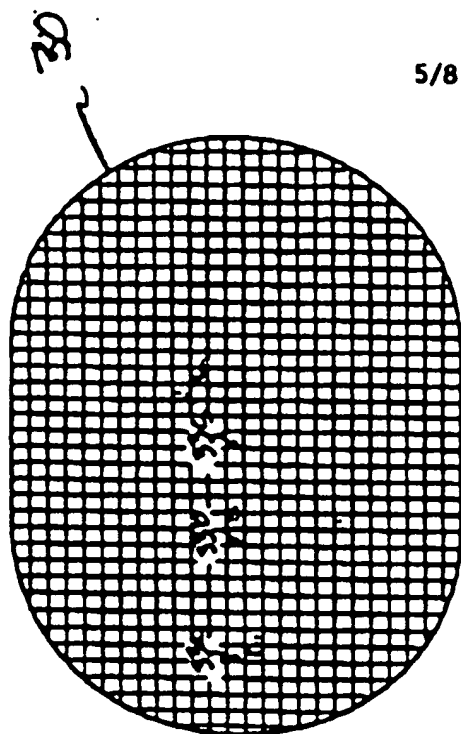


Fig. 6

BEST AVAILABLE COPY

Fig 5A

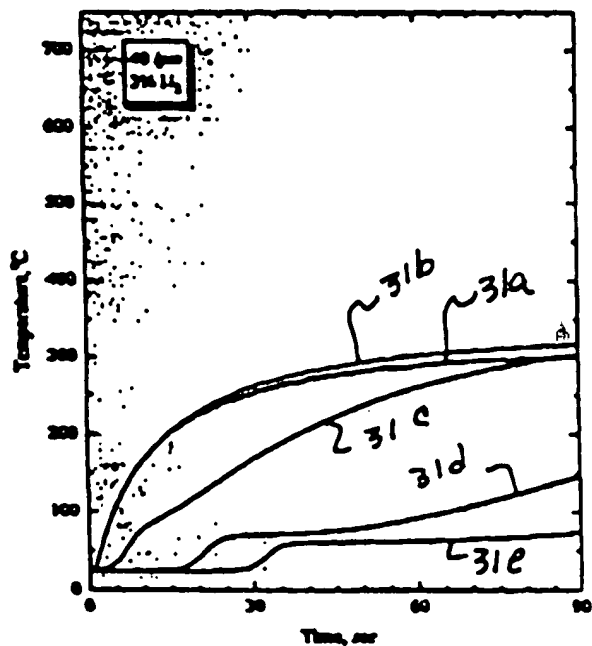


Fig 5B

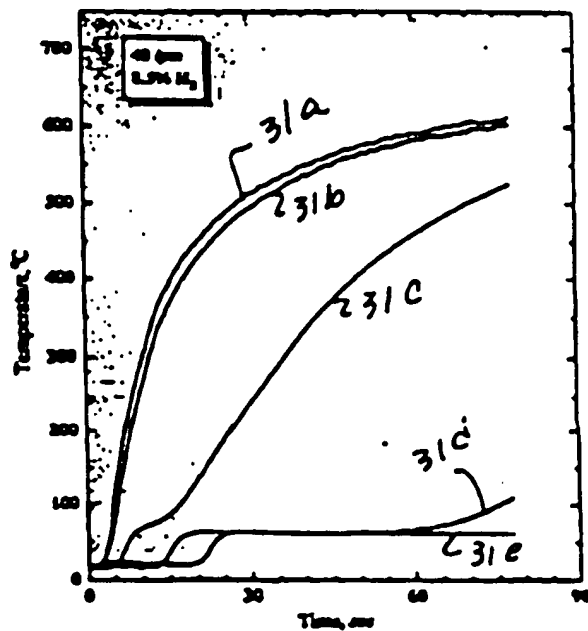
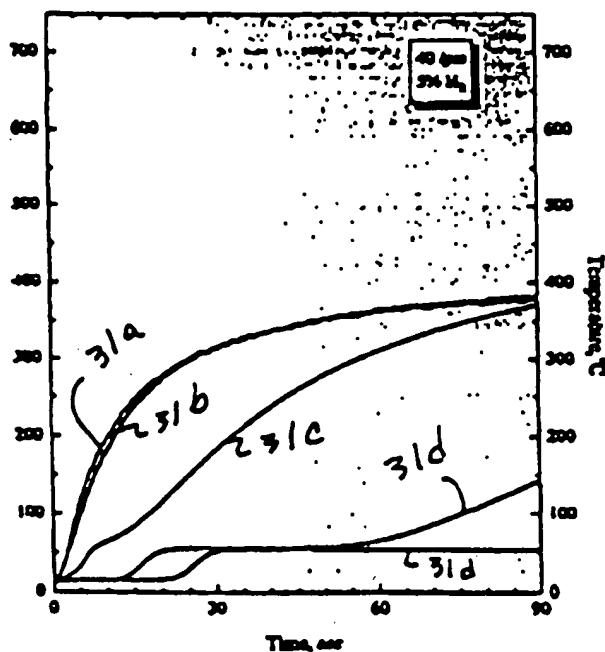


Fig 5C

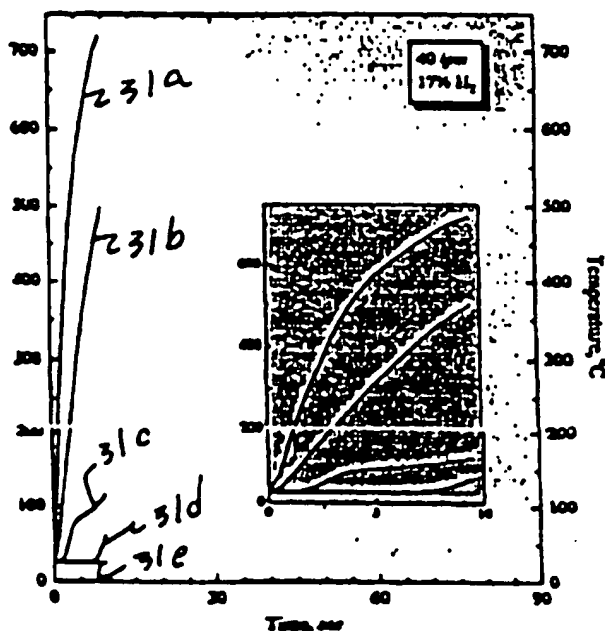


Fig 5D

7/8

Fig 6A

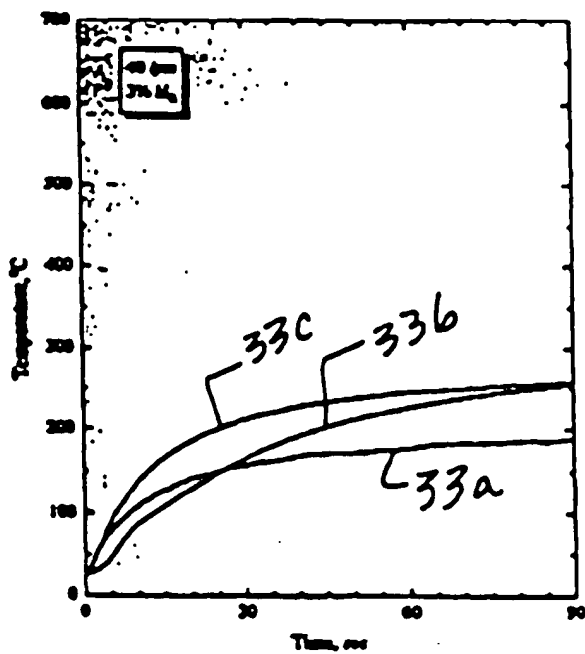


Fig 6B

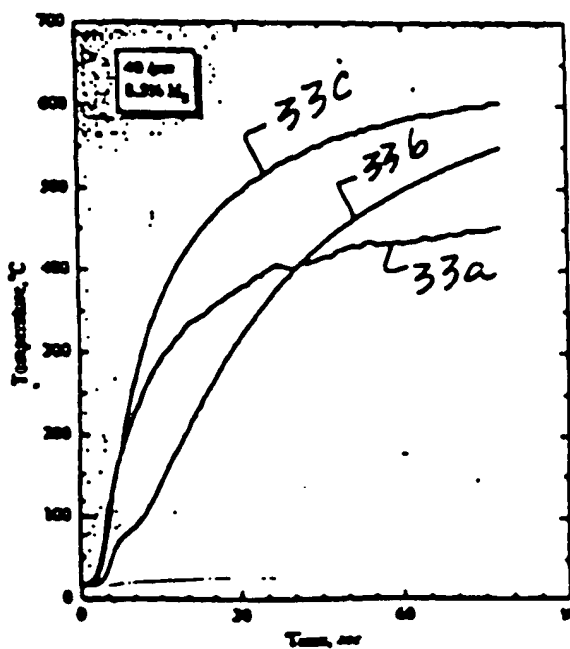
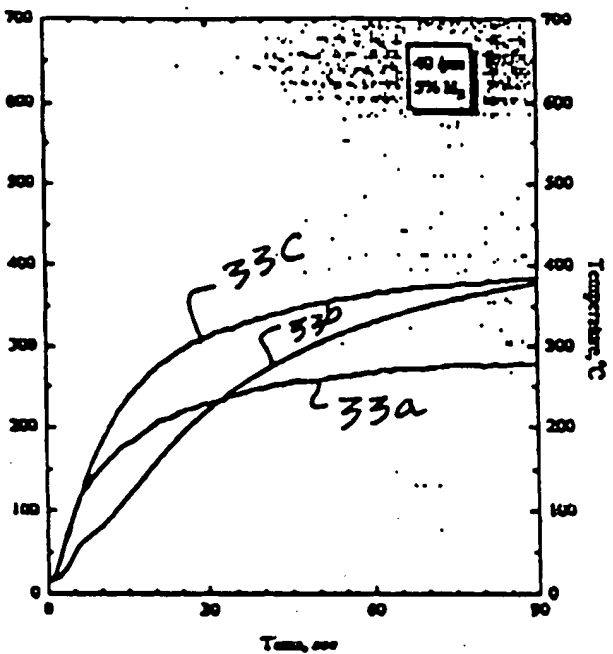


Fig 6C

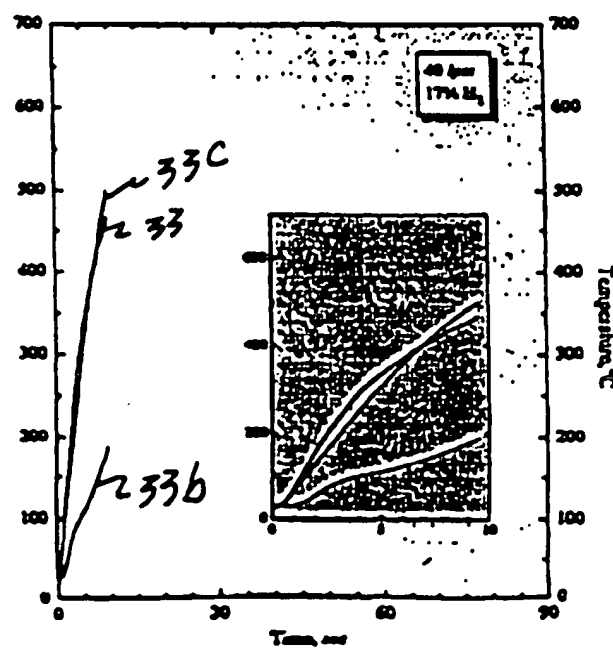


Fig 6D

8/8

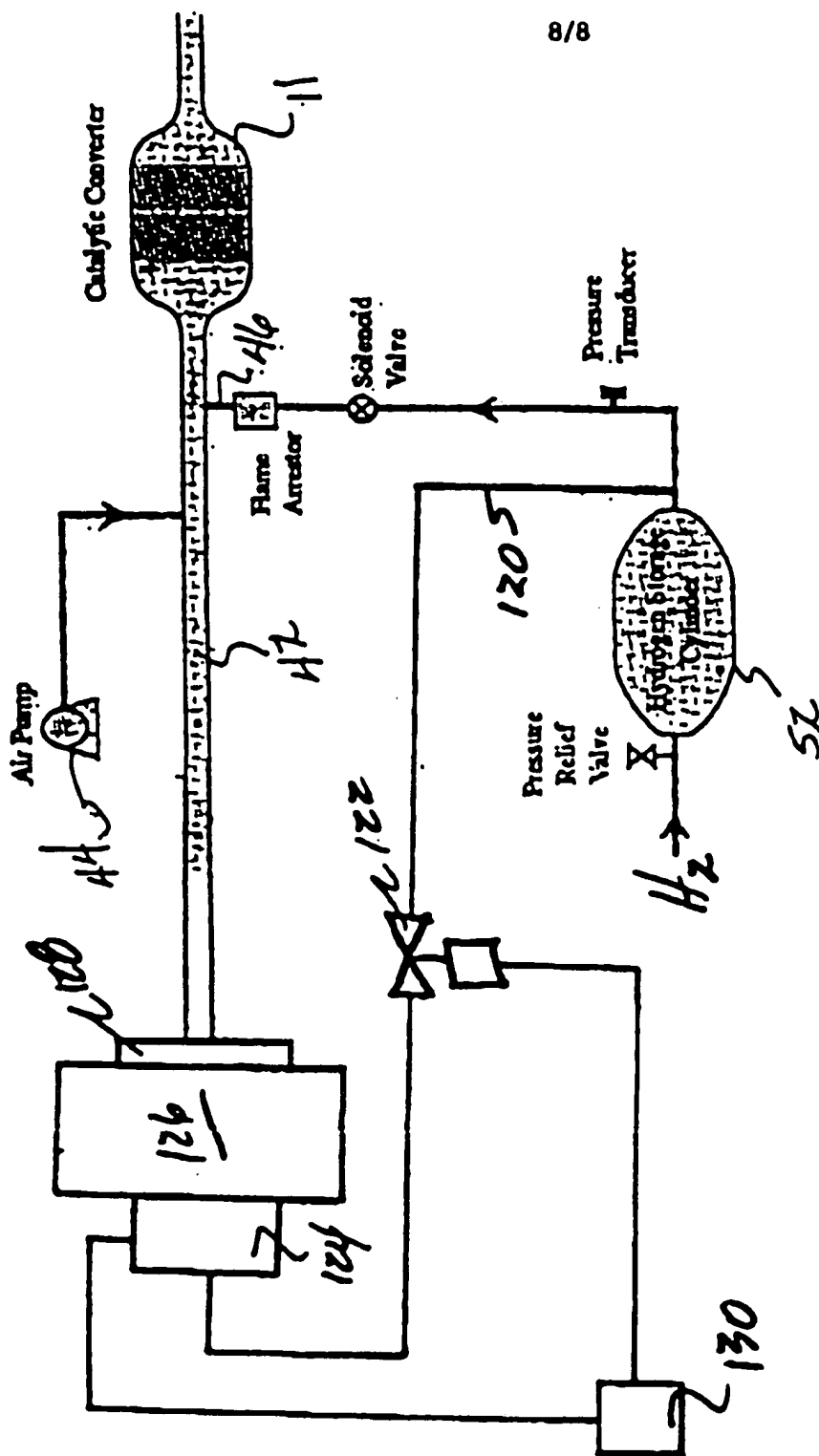


Fig 7

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 95/12912

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 F01N3/20 F02M25/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Maximum documentation searched (classification system followed by classification symbols)

IPC 6 F01N

Documentation searched other than maximum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,41 03 668 (BAYERISCHE MOTOREN WERKE) 13 August 1992	1-3,5,6, 8-10,16, 17,20,22
Y	see the whole document	7,11,13
Y	US,A,3 311 097 (MITTELSTAEDT) 28 March 1967	11
A	see column 1, line 15 - line 34 see column 3, line 37 - line 49; figure 1	18,19
Y	US,A,3 779 014 (NOHIRA) 18 December 1973	7,13
A	see column 3, line 6 - line 56; figures 1,2	1-3,6, 17,20
	--- -/-	

☒ Further documents are listed in the continuation of part C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" documents defining the general state of the art which is not considered to be of particular relevance
- "B" earlier document but published on or after the international filing date
- "L" documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" documents referring to an oral disclosure, use, exhibition or other means
- "P" documents published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to substantiate the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "Z" documents member of the same patent family

Date of the actual completion of the international search

29 January 1996

Date of making of the international search report

07.02.1996

Name and mailing address of the ISA

European Patent Office, P.B. 3618 Patentstein 1
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 631 opt. 41
Fax (+ 31-70) 340-3046

Authorized officer

Friden, C

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 95/12912

C(Communication) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 18 no. 249 (M-1604) ,12 May 1994 & JP,A,06 033748 (AISIN SEIKI CO LTD) 8 February 1994, see abstract	8-10,14, 15,17,22
A	---	1-4,6
A,P	DE,A,44 20 715 (MASCHINEN- UND ANLAGENBAU GRIMMA) 26 January 1995 see column 5, line 11 - column 7, line 60; figures 1-3	1-4,6, 9-11,14, 15,17,20
A	---	1,2,5,8, 9,16,17, 20,22
A	PATENT ABSTRACTS OF JAPAN vol. 17 no. 144 (M-1386) ,23 March 1993 & JP,A,04 318214 (TOYOTA MOTOR CORP) 9 November 1992, see abstract	
A	---	
A	DE,A,22 46 218 (VOLKSWAGENWERK AG) 28 March 1974	
A	---	
A	US,A,4 763 610 (THOMAS) 16 August 1988	
A	---	
A	FR,A,2 387 357 (TALENTI) 10 November 1978	
A	---	
A	US,A,4 332 219 (GONZALEZ) 1 June 1982 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/12912

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-4103668	13-08-92	NONE	
US-A-3311097	28-03-67	NONE	
US-A-3779014	18-12-73	NONE	
DE-A-4420715	26-01-95	WO-A- 9503480	02-02-95
DE-A-2246218	28-03-74	NONE	
US-A-4763610	16-08-88	AU-B- 5306686	29-07-86
		CA-A- 1272647	14-08-90
		EP-A, B 0207122	07-01-87
		WO-A- 8604117	17-07-86
FR-A-2387357	10-11-78	CA-A- 1071950	19-02-80
		CH-A- 629569	30-04-82
		DE-A- 2816115	02-11-78
		GB-A- 1554140	17-10-79
		JP-A- 53134793	24-11-78
US-A-4332219	01-06-82	US-A- 4450060	22-05-84

HP OfficeJet
Personal Printer/Fax/Copier

Fax Log Report for
Cynthia Seal
713-864-4794
Sep-18-98 09:59 AM

<u>Identification</u>	<u>Result</u>	<u>Pages</u>	<u>Type</u>	<u>Date</u>	<u>Time</u>	<u>Duration</u>	<u>Diagnostic</u>
Jeffrey L. Streets	OK	29	Sent	Sep-18	09:49A	00:10:24	0025c2030022
